DESIGN OF LARGE AREA PLEDS ON FLEXIBLE SUBSTRATES: HIGHLY EFFICIENT FLEXIBLE DEVICES USING A STATISTICAL COPOLYMER OF OXADIAZOLE-CONTAINING PPV

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1. ABSTRACT

With polymers as the active layer on a plastic substrate, construction of flexible devices is possible, although the use of calcium cathodes places stringent requirements on the encapsulation of the device. Our work focuses on the development of polymers that will function with higher work function cathodes, making encapsulation less problematic. Additionally, we seek to fabricate stable, flexible PLEDs with a simple device configuration for military display applications. To this aim we have made efficient multi-layered flexible PLEDs using a statistical copolymer of hole transporting dialkoxy-substituted PPV with an electron transporting oxadiazole containing PPV derivative as the emissive layer. Even in single layered devices, this polymer shows good performance. When PEDOT/PSS was coated on the ITO and LiF was evaporated between the emissive layer and Al, device efficiency is improved significantly. Several other cathode materials were also screened, and those results will be reported as well.

2. INTRODUCTION

In recent years, great progress has been made in developing conjugated polymeric materials for applications in optoelectronic devices, such as light emitting diodes (LEDs) (Friend *et al.*, 1999). These devices provide some added advantages over their inorganic counterparts. They exhibit good luminous efficiency and can be operated at low turn-on voltages. Color of the emitted light can be tuned by varying the polymer chemical structure or conjugation length. These materials may be made on a plastic substrate and thus offer the possibility for fabrication of flexible devices. Additionally, an all-polymer LED could be manufactured at lower cost and with ease (Friend *et al.*, 1999).

One of the most attractive features of PLEDs is their simple device configuration, illustrated in Figure 1. The device architecture consists of three basic components that are the anode, the cathode, and the polymer layer. In this device, holes are injected from the

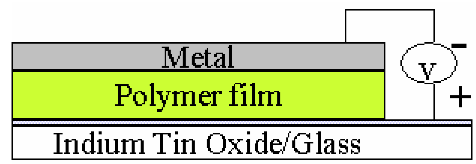

Figure 1. Device configuration of one layer polymer light emitting diode.

anode and electrons from the cathode. They then travel through the polymer film, recombine and lead to the formation of an exciton, the excited molecular state. When the exciton decays back down to the ground state, a photon of light is emitted. To enhance device performance, additional hole- and electron-injecting/transporting layers can be incorporated into the device construction (Friend *et al.*, 1999; Patel *et al.*, 2002).

Despite these attractive features, good stability of the emissive layer and of the device itself remain challenges. Poly(p-phenylenevinylene) (PPV), one of the most commonly used materials for the emissive layer, has phenyl rings connected by vinyl linkages. When exposed to oxygen, these vinyl linkages are oxidized to carbonyls, breaking the conjugation and hence degrading device performance (Papadimitrakopoulos *et al.*, 1994). Additionally, most metals used for the cathode, such as calcium, have a low work function, making them highly reactive with oxygen and moisture; device efficiency is again compromised. An encapsulated LED fabricated from a more stable emissive layer and cathode metal should be more stable and have a longer lifetime.

Another obstacle that must be overcome to optimize device performance is unbalanced electron and hole injection and transport. In PPV, like most organics, holes are more easily injected than electrons (Peng, Bao, and Galvin, 1998). This imbalance leads to recombination of charges close to the metal cathode,

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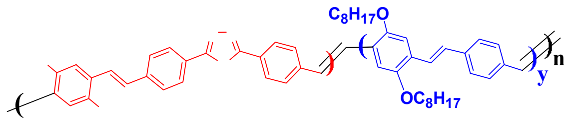

SC30

Figure 2. Structure of the statistical copolymer (SC30), which has on average 70% oxadiazole containing PPV monomer and 30% PPV monomer. Composition of the copolymer was deduced from NMR.

resulting in luminescence quenching and the consequent lowering of device efficiency (Becker *et al.*, 1997).

In this work, the primary objective is to fabricate a flexible large area PLED display with high device and luminous efficiencies for use in military applications. Additionally, aluminum is used for the cathode. A higher work function metal, aluminum can withstand exposure to oxygen and moisture for longer times, making expensive encapsulation techniques less necessary. Devices with calcium and gold as cathodes are also screened for comparison to devices with aluminum.

Table 1. Device efficiency and turn-on voltage values determined for PLEDs. (*) For these devices the PEDOT/PSS layer was optimized to a thickness of 120nm.

Finally, development of a polymeric material that is less susceptible to oxidative degradation and balanced charge injection and transport is desired. To this end, a statistical copolymer containing PPV with solubilizing dialkoxy groups and a PPV derivative with oxadiazole moieties (SC30) has been designed and used for the emissive layer (see Figure 2). Based on prior work, it is known that oxadiazoles, when incorporated into a PPV backbone, improve electron injection and result in better charge balance in the emissive, semiconducting layer (Peng, Bao, and Galvin, 1998). These moieties are also electron deficient and draw electron density away from neighboring vinyl bonds, rendering them less vulnerable to degradation upon exposure to oxygen (Peng, Bao, and Galvin, 1998). SC30 has been used in this experiment to further promote device stability and efficiency.

3. EXPERIMENTAL

The synthesis, structural characterization, and photophysical properties of SC30 are reported elsewhere (Vaidyanathan and Galvin, 2004). It is a statistical copolymer of 70 % oxadiazole substituted PPV and 30 % PPV. In a single layer LED with aluminum as the cathode, SC30 has an external quantum efficiency of 0.15 %. A luminance of 544 cd/m^2 is obtained at a current density of 160 mA/cm^2 (20 V) (Vaidyanathan

Device Configuration	External Quantum Efficiency (%)	Turn-on Voltage (V)
Glass/ITO /PEDOT/SC30/Au	0.005	18
Plastic/ITO /PEDOT/SC30/Au	0.015	6
Glass/ITO/PEDOT/SC30/Ca	0.28	4
Plastic/ITO /PEDOT/SC30/Ca	0.2	6
Glass/ITO/PEDOT/SC30/Al	0.23	6
Plastic/ITO/PEDOT/SC30/Al	0.1	7
Glass/ITO/PEDOT/SC30/LiF/Al*	0.8	4
Plastic/ITO/PEDOT/SC30/LiF/Al*	1	4

Table 1. Device efficiency and turn-on voltage values determined for PLEDs. (*For these devices the

and Galvin, 2004). Single and multiple layered devices were made, using ITO as the anode on either glass or poly(ethylene terephthalate) (PET) flexible substrates. These films were obtained from Innovative Specialty Films and had a sheet resistance of 100 Ω per square. Multiple layer devices were made using PEDOT/PSS, poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate), as the hole- injecting/transporting layer. The PEDOT/PSS (Baytron P grade) was obtained from Bayer Chemicals and was spin-coated over the ITO. Prior to spin coating the PEDOT/PSS layer, the ITO anode was cleaned according to a protocol obtained from Bayer Chemicals (for more information, see http://www.bayer-echemicals.com/request/pages/baytron/a_oled.html). On flexible ITO substrates, which can be microscopically rough, PEDOT/PSS also serves as a planarizing layer. The SC30 was dissolved in freshly distilled 1,1,2,2-tetrachloroethane and spin-coated onto the ITO layer at a

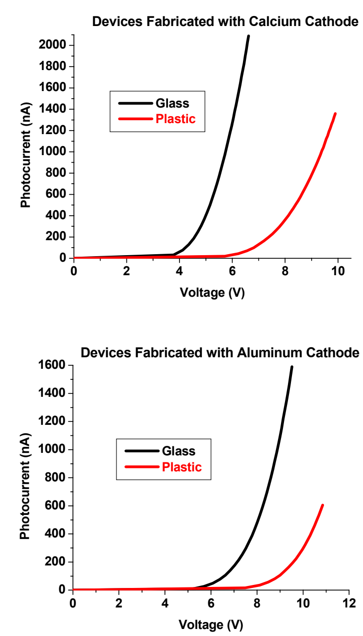

Figure 3. Devices efficiencies made with PEDOT/PSS hole transporting layer (a) using calcium for the cathode (b) using aluminum for the cathode.

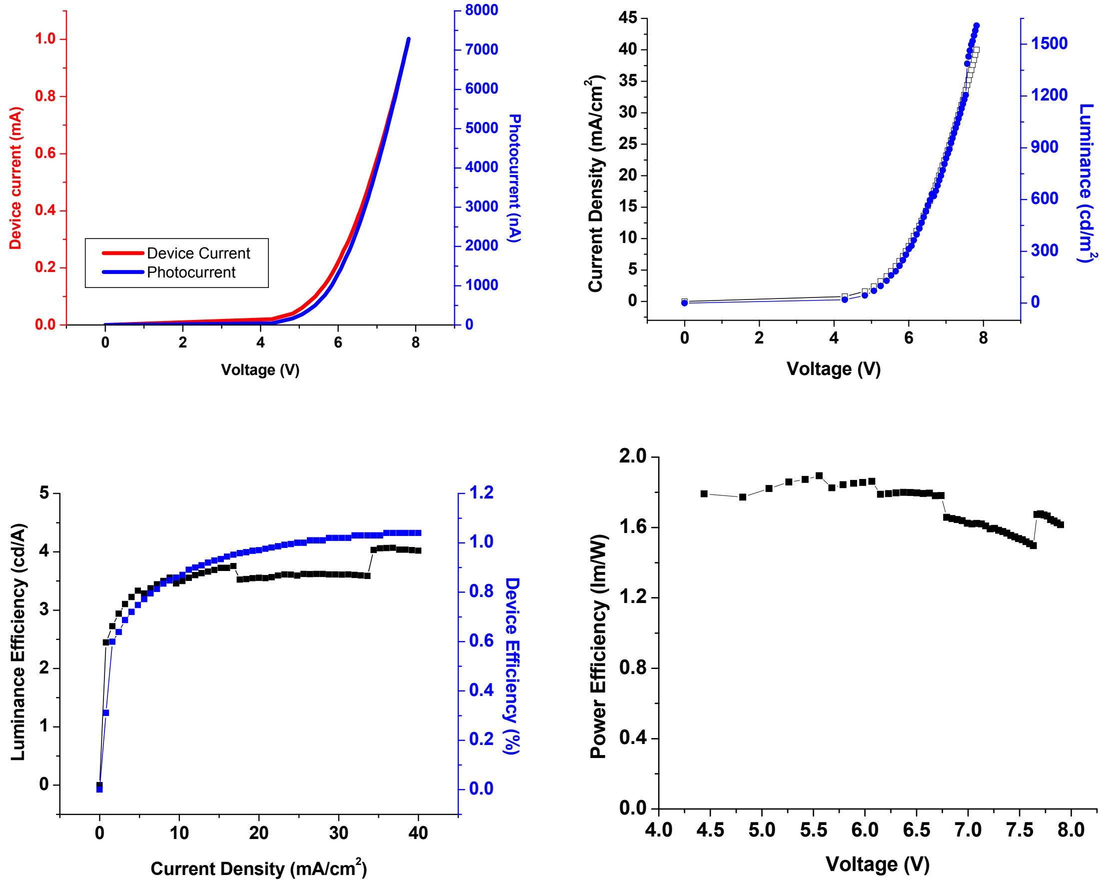

Figure 4. Characteristics of device made on plastic substrate with PEDOT/PSS , LiF and aluminum cathode (a) device current versus photocurrent, (b) brightness in cd/m^2, (c) external quantum and luminance efficiencies and (d) power efficiency.

rate of *ca*. 900 rpm for 120 s resulting in a film of *ca*. 100nm in thickness. To aid electron injection, an 8-10 Å layer of lithium fluoride was evaporated under reduced pressures over the SC30 layer for some devices. The cathode (either aluminum, gold or calcium) was shadow evaporated onto the substrate defining pixels of 1 mm radius. Current-voltage characteristics were measured using a HP 4155B Semiconductor Parameter Analyzer. Brightness measurements were done using a TRICOR Inc. Model 820 Video Photometer and analyzed using Eyeppearance 3.67 software.

4. RESULTS AND DISCUSSION

Efficiencies and turn-on voltages for all devices fabricated are presented in Table 1. Surprisingly, device made with the gold cathode worked despite the large electron injection barrier (Bernius *et al.*, 2000). This can be attributed to the lowering of the LUMO levels of the copolymer with the incorporation of oxadiazoles (Peng, Bao, and Galvin, 1998). As expected, devices with calcium cathodes performed best overall (Figure 3a). The devices with aluminum cathodes also worked well (Figure 3b), but the performance greatly improved with the addition of the LiF layer. The device on plastic showed an exceptionally good external quantum efficiency of 1 %, with a low turn-on voltage of 4 V and over 7 μA photocurrent at 1 mA device current. This device also showed a brightness of 1200 cd/m^2 at 8 V and 40 mA/cm^2. This translates to luminance and power efficiencies reaching 3 cd/A and 1.4 lm/W, respectively.

To improve the processing of the SC30 layer, a lower molecular weight SC30 was synthesized and used for device fabrication (M_n of 2490 g/mol, M_w of 4160 g/mol, and polydispersity of 1.67). The devices with aluminum cathode and LiF layer did not show an increase in external quantum efficiency (Figure 4a and 4c). However, the brightness increased to 1600 cd/m^2 at 8 V and 40 mA/cm^2 (Figure 4b). Consequently, the luminance and power efficiencies increased to 4 cd/A and 1.8 lm/W, respectively (Figure 4c and 4d).

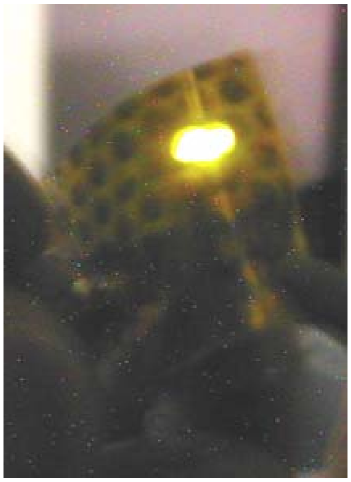

Figure 5. Functional multiple layer flexible device based on RC30.

Issues arising from oxidative stability have not yet been studied. Aluminum was chosen as the cathode material specifically because it is not as reactive in air as calcium. For this reason the good performance of devices made using aluminum are especially encouraging.

CONCLUSIONS

Several cathodes were screened to make flexible LEDs using a soluble PPV and oxadiazole substituted PPV derivative statistical copolymer. For all devices, a hole transporting PEDOT/PSS layer was used. It was found that LEDs could be fabricated using even gold cathodes. With calcium as the cathode, performance greatly improved as expected. Devices made with a lithium fluoride injecting layer and aluminum cathode further improved external quantum, luminance, and power efficiencies. Finally, a long-range goal of fabricating a large area flexible device is planned to test the feasibility of making a relatively large-scale device on a flexible substrate.

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